Zero Electron Kinetic Energy (ZEKE) Photoemission
of CH_4 and CD_4
at the Carbon K Ionization Threshold

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Abstract:

Zero Electron Kinetic Energy (ZEKE) photoemission was applied to examine the vibrational fine structure in the C 1s core line of methane. The line broadening from the post collision interaction (PCI) could be understood using the threshold lineshape of atomic argon. From a Franck-Condon analysis of the CH_4 and CD_4 ZEKE spectra, the geometry of core-ionized methane was evaluated. The equilibrium bond length was determined to be contracted by 0.052(7) Å from the ground state of methane (1.085 Å). Our results agree with the x-ray photoelectron spectroscopy (XPS) experiment of Gelius, showing in addition that the molecular structure determined from the vibrational structure in core-level photoemission does not depend on the photoelectron kinetic energy.

Introduction:

A photoemission transition can lead to molecular ions in various vibrational and rotational final states. For core photoemission only the vibrational information is accessible because the core hole lifetime is short enough ($\sim 10^{-14}$ s) that the natural linewidth (~ 0.1 eV) is larger than any rotational energy separations. The vibrational fine structure can help to determine the equilibrium geometry of the molecular ion, as in valence-level photoemission. The change in the molecular geometry results from a balancing of electric forces. The bond order is unaltered, since core orbitals are non-bonding. In the

equivalent-core approximation, ejection of a core electron is equivalent to increasing the nuclear charge by one, which taken alone, will repel the other nuclei. However, the remaining electrons will relax toward the core hole, tending to reduce the size of the molecule both directly and indirectly by shielding the core hole, thereby ameliorating the added internuclear repulsion. From the vibrational fine structure one can make qualitative inferences about the extent of electronic relaxation.

Vibrational excitation contributes to photoemission lineshapes in isolated molecules, adsorbates on surfaces, and solids. Recently, Nilsson and Martensson[1] in a temperature-dependent study, suggested that for adsorbates the linewidth results more from vibrations rather than from electronic excitations. For gas-phase molecules, the contribution of different vibrational states to the lineshape can be observed more directly because the lifetimes are longer and, except for rotations, there are no other contributions.

Previous work on vibrationally resolved core transitions has mainly been devoted to resonances, in which the core electron is excited to an anti-bonding or Rydberg orbital. These studies have been carried out both by electron impact[2] and by photoabsorption.[3,4] Randall et al.[5] demonstrated the influence of vibronic coupling in the C $1s^{-1}$ below-threshold resonances of CH_4. Compared with photoionization, the presence of an additional electron makes the situation in resonant absorption more complicated, and additional vibrational modes may be active. Using monochromatized Al Kα radiation, Gelius[6] observed vibrational structure in the C $1s^{-1}$ core photoelectron peak of CH_4. The C-H bonds were determined to be contracted by 0.05 Å in the ion.

In the present experiment, Zero Electron Kinetic Energy (ZEKE) photoelectron spectroscopy was used to study the C $1s^{-1}$ photopeaks of CH_4 and CD_4. The ionic geometry was evaluated from Franck-Condon analyses of the vibrational peak separations and intensities. A higher experimental resolution was achieved than in Gelius's experiment, allowing a more accurate determination of the bond length. In addition, a

comparison of the results from the near-zero and higher kinetic-energy spectra tests whether the separation of electronic and nuclear motion is valid at the ionization threshold. Finally, the isotopic shift in the vibrational energy permits sampling the ionic potential at different heights. During the same measurement period, ZEKE photoelectron spectra were also collected from N_2 and CO. That work is being presented separately.[7]

Experimental:

These experiments were performed at the Dragon monochromator,[8] U4B, at the UV ring of the National Synchrotron Light Source (NSLS). A ZEKE electron analyzer, using a weak electric field and time-of-flight, detected electrons of kinetic energies between 0 and 30 meV.[9] This type of electron analyzer offers high resolution with much better sensitivity than angle-resolved analyzers. During the measurements the UV ring was operated in single-bunch mode. The electron analyzer was oriented at 90° relative to both the photon polarization vector and an effusive gas jet. Because of the large angular acceptance of the analyzer, its orientation is not expected to have a significant effect. The vacuum of the chamber was isolated by a 1000 Å thick titanium window from a UHV chamber upstream and from the beam line. From fitting the spectra, the total experimental resolution is estimated to be 0.15 eV. This width is considerably smaller than C-H (~0.4 eV) or C-D (~0.3 eV) symmetric-stretch energy spacings.

Results and Discussion:

Post collision interaction (PCI) changes core photoemission lineshapes. PCI refers to the energy transfer between a photoelectron and an Auger electron. It has the largest effect at threshold, where this experiment was performed. To analyze the influence of PCI without vibrational effects, spectra were collected of atomic argon, as shown in Figure 1. In these spectra the photon energy was calibrated by placing the methane 1s - t_2 3p resonance at 288.00 eV, the energy value from the electron impact work of Tronc et al.[2]

The electron count rate was normalized to an I_0 signal from a gold grid, on to which gold was evaporated in vacuum. Resonances were observed below the ionization threshold from the double Auger decay of excited states $2p_{1/2}^{-1}(Rydberg)$[1]. The photoemission line maximum is shifted above the threshold, broadened, and given a high photon energy tail by PCI. The PCI lineshape reflects the probabilities for the photoelectron to lose different amounts of energy to the Auger electron.

In Figure 1 the solid curve represents a fit with the PCI line profile from Niehaus[10] convoluted with a gaussian broadening of 0.15 eV. More recently an improved calculation of PCI by Russek and Mehlhorn[11] included the 'no passing' effect, that is the time for the Auger electron to overtake the photoelectron. However, the quality of the fit obtained with the Niehaus lineshape shows that its approximations are viable at threshold. From our analysis with the Niehaus lineshape, a lifetime width for the argon 2p hole of 0.14(1) eV was obtained in fair agreement with the value of 0.12(1) eV obtained in earlier work by us[12] and with the electron impact experiment values of 0.14(1) eV and 0.13(1) eV for the $2p_{3/2}$ - 4d and $2p_{1/2}$ - 4d resonances, respectively.[13] Interestingly, the lowest energy resonances were determined to have slightly longer lifetimes than the higher resonances or than the ionized hole state.[13]

From the analysis of the Ar $2p_{1/2}$ spectrum, the Niehaus lineshape can be applied confidently to the individual vibrational components of the methane C $1s^{-1}$ peak. The broadening of ZEKE core lines from PCI (~0.5 eV FWHM) is larger than the experimental resolution. This PCI broadening limits this method to molecules with one or two allowed vibrational modes. For more complex molecules higher kinetic-energy photoelectron spectroscopy should be used.

The methane spectrum is shown in figure 2, and a deuterated methane spectrum in figure 3. Three vibrational components are needed to fit the data in each case. The solid

curve displays a fit with PCI lineshapes for each vibrational subpeak, and with Lorentzians for the Rydberg resonances. In methane a surprising intensity of ZEKE electrons is present in the high-lying Rydberg resonances, more than is observed in Ar, N_2 or CO.[7] As expected CD_4^+ has a smaller vibrational energy spacing than CH_4^+, by $\sqrt{2}$.

The intensities and energy separations of the three vibrational components were obtained from fits of both the CH_4^+ and CD_4^+ spectra. In this case of C $1s^{-1}$ ionization of methane the assignment of these peaks is simple, because only one of the nine vibrational modes is active. Because a positive charge is created on the central carbon atom, only the v_1 symmetric C-H stretch can be excited. A harmonic potential was assumed in our fits: this approximation is reasonable because only states deep in the potential well are involved. Here, v=0 for the ground state and v=0,1,2 for the final state. When an anharmonic term was included, the result changed less than the experimental error. A conversion is necessary from a normal coordinate to a bond length. For methane it is given by

$$\xi = 2\sqrt{m}\, r,$$ where ξ is the normal coordinate, m the mass of H (or D) and r the bond distance C-H (C-D).

The best agreement between a Franck-Condon calculation and the experimental spectra of CH_4^+ and CD_4^+ yields a C-H (or C-D) bond length contracted by 0.052(7) Å, which is an averaged value combining the results for both CH_4^+ and CD_4^+. The contraction of the molecule upon C 1s ionization implies that the relaxation of the valence electrons toward the hole outweighs the added repulsion between the protons and the C nucleus together with its core electrons. This result may be general for core ionization: we note that both N $1s^{-1}$ N_2 ($\Delta r = -0.02(1)$ Å) and C $1s^{-1}$ CO ($\Delta r = -0.057(5)$ Å) have shorter internuclear distances compared with the neutral molecules.[7]

Our value for the C-H bond contraction agrees with the early work of Gelius et al.,[6] based on monochromatized Al $K\alpha$ radiation and a large hemispherical analyzer.

Comparing their experiment with the calculation of Meyer,[14] who derived a potential as a function of the symmetric C-H stretch displacement, Gelius et al. obtained $\Delta r = -0.05$ Å. That the ZEKE and XPS results agree implies that there is no dependence on the electron kinetic energy. This confirms the validity of the separation of electronic and nuclear degrees of freedom, which is assumed in the Franck-Condon analysis.

In the equivalent core model, the analog for CH_4^+ $1s^{-1}$ is the common solvent ion NH_4^+. Using high resolution laser methods, Crofton and Oka[15] have studied the individual rotational peaks in the ν_3 band of gaseous NH_4^+ in the ground electronic state. Their result for the equilibrium bond length $r_e(NH_4^+)$, 1.021(2) Å, is similar to our value for $r_e(CH_4^+$ $1s^{-1})$, 1.033(8) Å, which is obtained using $r_e(CH_4)$, 1.085(1) Å.[16] However, the small difference between the two ions is also significant. Slightly longer bonds were observed for both the core-ionized CO^7 and the core-excited N_2^{17} molecules compared with their equivalent core molecule NO. In a qualitative way, this descrepancy in the equivalent core approximation can be understood from the small, but finite size of the core 1s orbital. NH_4^+ has both an additional 1s electron and nuclear charge. In the region of space occupied by the 1s orbital, the valence orbitals will have more attractive potentials leading to somewhat contracted valence orbitals and slightly shorter bonds than CH_4^+ $1s^{-1}$.

A broad satellite peak was observed at 306(1) eV binding energy. This peak might be assigned to states with the configuration C $1s^{-1}$ $1T_1^{-1}$ $2T_2^1$, which have a hole in the highest occupied orbital and an additional electron in the lowest unoccupied orbital. For CO and N_2 $\pi - \pi^*$ satellites, Schirmer et al.[18] calculated a number of electronic final states from the various possible angular momentum couplings between the holes and electron. It is also probable for methane that the width of the satellite peak, 5 eV, results mainly from the presence of different electronic states.

Conclusion:

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Carbon 1s   Electron Kinetic Energy (ZEKE) photoel

of CH_4 and CD_4 with vibrational resolution. Post-Collision

broadening to the threshold lineshape, which however can be

function of Niehaus.[10] The C-H (or C-D) equilibrium bond

molecule is contracted by 0.052(7) Å compared with the grc

agree with the earlier XPS measurement of Gelius,[6] suggest

for the ion does not depend on the detected photoelectron kir

of C $1s^{-1}$ CH_4^+, which reflects the amount of electronic rel

case of N 1s ionization of N_2 and slightly less than in the ca

But in all three cases the molecules shrink upon core photoe

changes are relatively small, < 0.1 Å.

Footnotes:

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Table I: Results from fitting the core photoemission lin Franck-Condon analysis.

	Binding Energy (eV)	Hole Width (eV)	ΔE_{vib}
CH_4^+ C $1s^{-1}$	290.70(3)	0.12(1)	0.39(2)
CD_4^+ C $1s^{-1}$	290.69(3)	0.12(1)	0.29(2)

Figure Captions

Fig. 1 ZEKE photoemission spectrum of argon at the $2p_{1/2}$ threshold. The solid line

represents a fit with Lorentzian lineshapes for the resonances and a Niehaus[10]

lineshape for the PCI broadened threshold peak.

Fig. 2 ZEKE photoemission spectrum of methane at the C 1s threshold. The solid line

represents a fit using the same lineshape functions as in the case of atomic argon.

The dashed lines show the vibrational components of the threshold peak. For each

vibrational component the peak intensity is shifted by PCI by about 0.2 eV from the

threshold energy.

Fig. 3 ZEKE photoemission spectrum of deuterated methane at the C 1s threshold. The
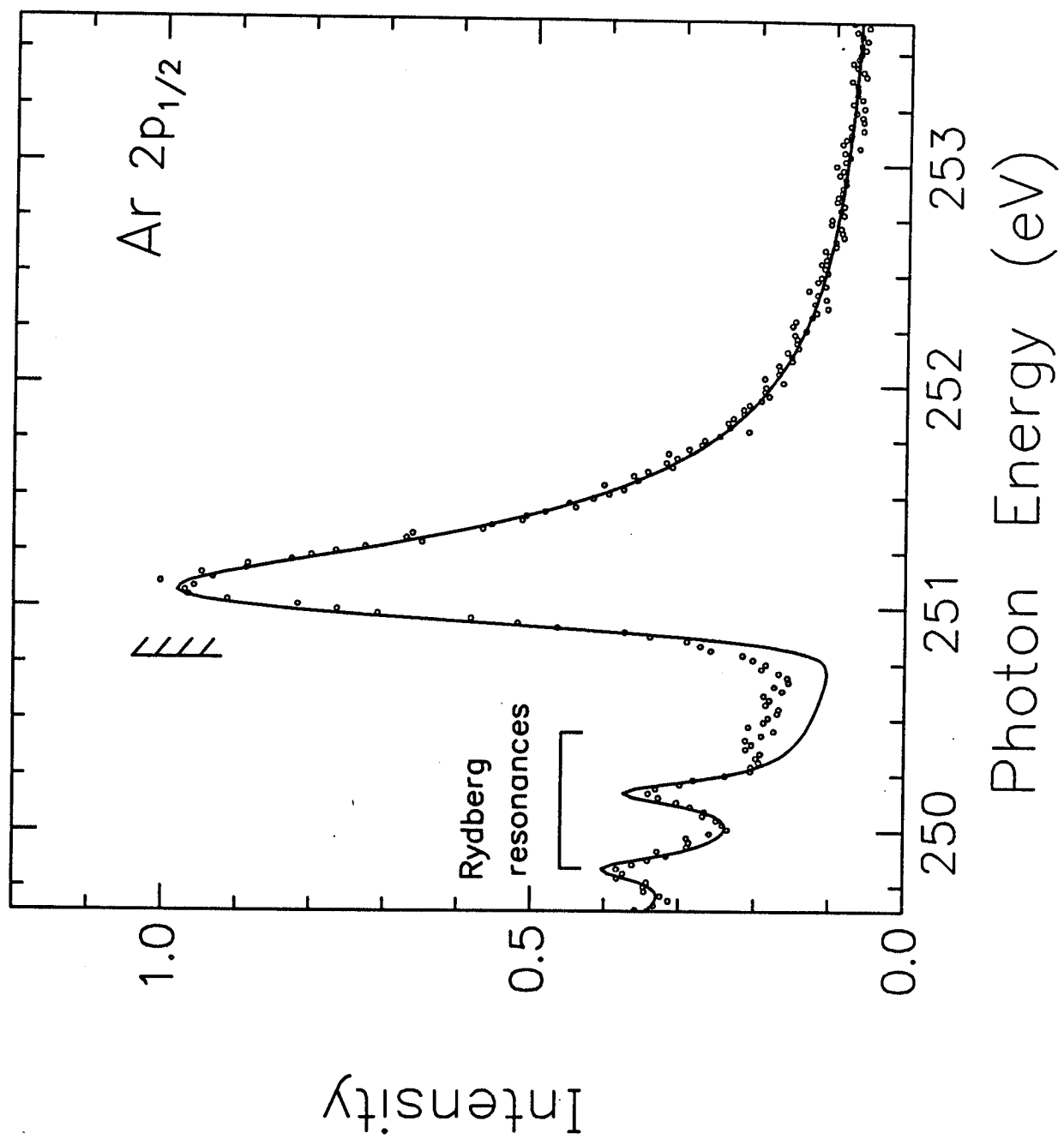
solid line displays a fit, and the dashed lines show the v= 0,1,2 components of the
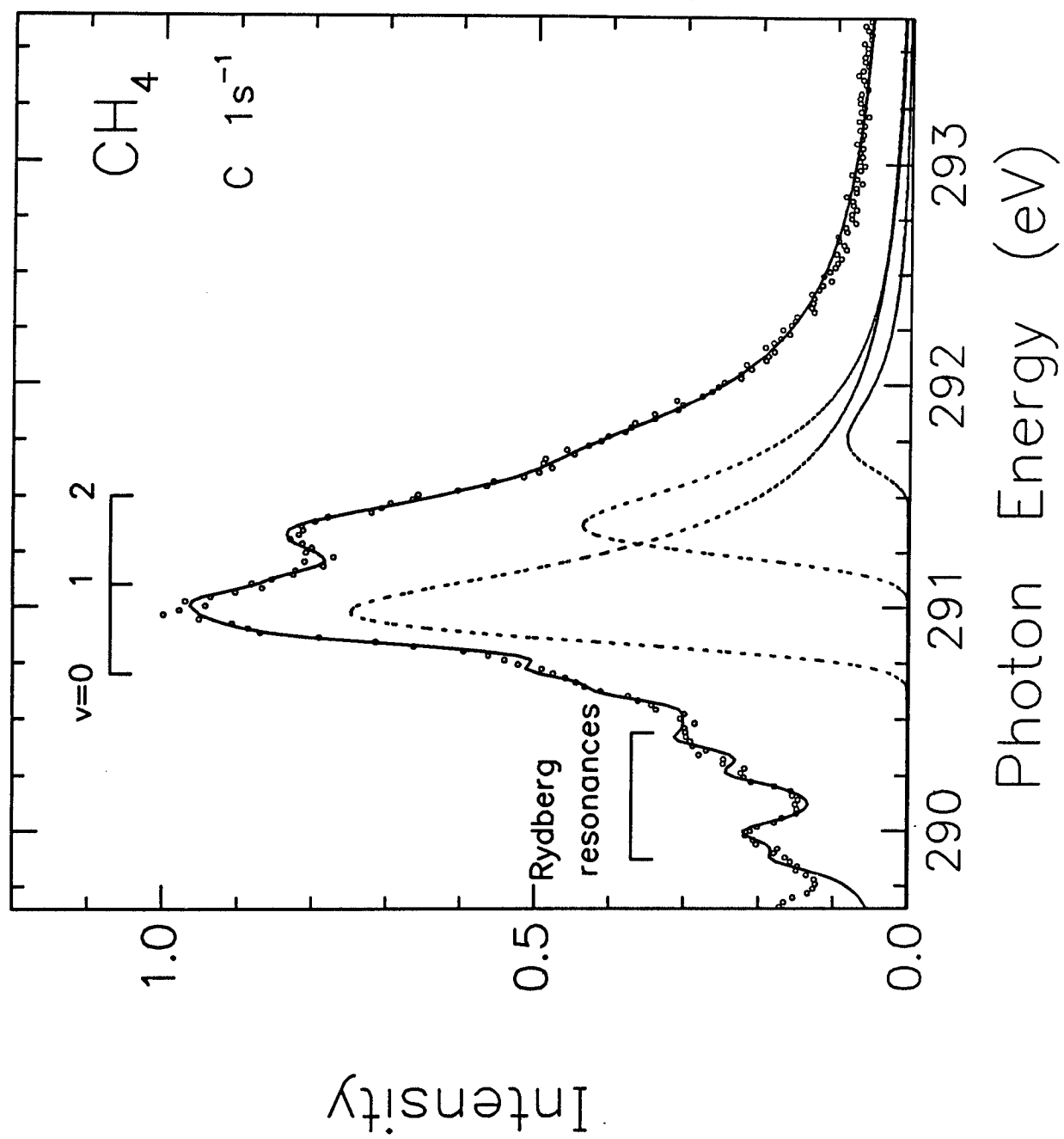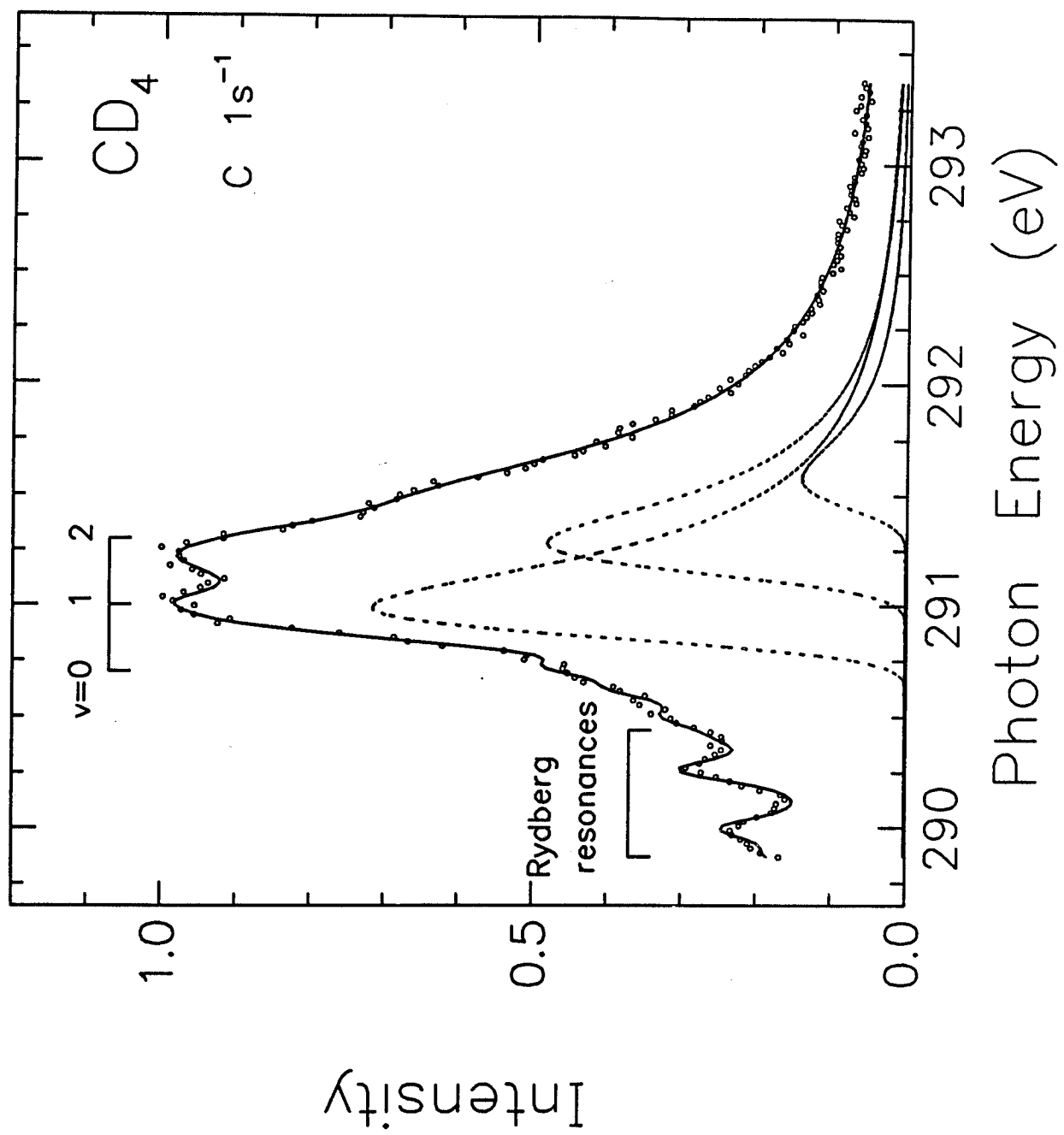
threshold peak.

Figure 1

Figure 2

Figure 3